

Transport and Elastic Properties of Fractal Media

Anthony P. Roberts

Faculty of Environmental Sciences,
Griffith University, Nathan, Qld. 4111, Australia

Mark A. Knackstedt

Department of Applied Mathematics,
Research School of Physical Sciences and Engineering,
Australian National University, Canberra ACT 0200, Australia

October 1995

Abstract

We investigate the influence of fractal structure on material properties. We calculate the statistical correlation functions of fractal media defined by level-cut Gaussian random fields. This allows the modeling of both surface fractal and mass fractal materials. Variational bounds on the conductivity, diffusivity and elastic moduli of the materials are evaluated. We find that a fractally rough interface has a relatively strong influence on the properties of composites. In contrast a fractal volume (mass) has little effect on material properties.

1 Introduction

In the past decade a number of important natural and manufactured materials have been shown to exhibit microstructures with fractal characteristics. For example, it has been shown that sedimentary rocks have internal surfaces that exhibit fractal roughness and in some cases the fractal regime may include the entire pore volume [1]. This geometric complexity has a number of important implications for transport properties in porous rocks. In another example it was shown that fractured surfaces of metals are fractal in nature and proposed that the fractal dimensions of the surfaces could be correlated to the impact energy of the sample [2]. Finally low-weight polymeric gel materials (aerogels) give a unique combination of properties; low-density and insulative, yet mechanically strong [3]. Aerogels are good examples of fractal materials, made up of clusters generated from the aggregation of primary particles [4].

While the concept of a fractal geometry provides a description of disordered material structure, it is not clear if the properties of these materials are affected by fractal characteristics nor how one may design and optimise fractal structure for a given application. Microstructural characteristics other than fractal dimension (e.g., connectivity, coordination) may be more important when deriving Structure-Property relationships. For example, in aerogels, the macroscopic connectivity at low density is the key microstructural characteristic associated with the mechanical strength of the material.

To date there has been no explicit investigation of the influence of fractal structure on material properties. Theoretical studies [5, 6, 7, 3, 8] have relied on simplistic models of fractal microstructure. In general the relationship of such models to real materials is unclear, and the predictive ability of the models is qualitative in nature. In this paper we investigate the influence of fractal structure on material properties. We find that a fractally rough interface has a strong influence on material properties. A fractal volume, in contrast, has little effect on properties.

2 Evaluation of Bounds

For general random composites there is no exact method of predicting properties. However a number of rigorous bounds, which depend on the microstructure of the composites, have been derived. These include bounds on the conductivity [9, 10] and the bulk [11] and shear [12, 13] moduli of composite materials (reviewed in Ref. [14]). The bounds are expressed [15] in terms of the volume fractions and properties of each of the phases and two microstructure parameters:

$$\zeta_1 = \frac{9}{2pq} \int_0^\infty \frac{dr}{r} \int_0^\infty \frac{ds}{s} \int_{-1}^1 du P_2(u) \left(p_3(r, s, t) - \frac{p_2(r)p_2(s)}{p} \right) \quad (1)$$

$$\eta_1 = \frac{5\zeta_1}{21} + \frac{150}{7pq} \int_0^\infty \frac{dr}{r} \int_0^\infty \frac{ds}{s} \int_{-1}^1 du P_4(u) \left(p_3(r, s, t) - \frac{p_2(r)p_2(s)}{p} \right) \quad (2)$$

where $p_3(r, s, t)$ is the three point correlation function [16], $t^2 = r^2 + s^2 - 2rsu$ and $P_n(u)$ denotes the Legendre polynomial of order n . Until recently the use of the bounds has been restricted to ‘particulate’ media, such as uncorrelated overlapping spheres [14]. Such models have limited utility in describing the microstructure of composite materials. We have shown that microstructure generated from level cuts of a random standing wave mimics the microstructure of a wide range of real composite materials including polymer blends [17], porous rocks [18] and foamed solids [19]. We have subsequently evaluated the bounds for a variety of level-cut microstructures and shown that it is possible to correlate quantitatively the effective physical properties of materials to their microstructure [17, 19]. Berk [20] has shown how the level-cut scheme may be used to model fractal interfaces, and the extension to volume fractals is simple. Here we investigate the properties of these surface- and volume-fractal materials using rigorous bounds. This allows us to investigate the influence of fractal structure on material properties.

A key quantity in the characterization of two phase materials is the two-point correlation function, $p_2(r) = p(1 - p)\gamma(r) + p^2$, where p is the volume fraction of the first phase and $\gamma(r)$ is the normalized correlation function with $\gamma(0) = 1$, $\gamma(\infty) = 0$. Physically p_2 gives the probability that two points a distance r apart will lie in the first phase. Two principle fractal types are evident in composites: surface and volume (or mass) fractals. Each can be characterized by the behaviour of the normalized correlation function $\gamma(r)$. Surface fractal behaviour occurs when the interface between the phases is rough at all scales. In this case Bale and Schmidt [21] have shown that $1 - \gamma(r) \sim r^{3-D_s}$ as $r \rightarrow 0$ where $2 \leq D_s < 3$ is the surface-fractal dimension. Experimental techniques have determined that a variety of materials exhibit fractal surfaces with $D_s > 2$. These include crushed glass, zeolites [22], silica gels [22, 23], lignite coals [21], porous rocks [1], soils [24] and composite steels [2] (see Korvin [25] for a review). On the other hand, volume (or mass) fractals occur when voids (or inclusions) are present at all scales. In this case $\gamma(r) \sim r^{-(3-D_v)}$ as $r \rightarrow \infty$ where $D_v < 3$ is the volume-fractal dimension [4, 26]. Fractal behavior of this type has been observed in silica gels [4, 27, 28] and soils [24].

3 Model morphologies: The level cut Gaussian random field

Random composites with a wide variety of morphological properties can be generated by taking level-cuts of a Gaussian random field (GRF). A simple definition of a GRF is

$$y(\mathbf{r}) = \sqrt{\frac{2}{N}} \sum_{i=1}^N \cos(k_i \hat{\mathbf{k}}_i \cdot \mathbf{r} + \phi_i) \quad (3)$$

where ϕ_i is a uniform deviate on $[0, 2\pi)$ and $\hat{\mathbf{k}}_i$ is uniformly distributed on a unit sphere. The magnitude of the wave vectors k_i are distributed on $[0, \infty)$ with a probability (spectral) density $P(k)$ ($\int P(k)dk = 1$). A composite material can then be defined by taking the region in space where $\alpha \leq y(\mathbf{r}) \leq \beta$ as the first phase, while the two regions contiguous to this $y(\mathbf{r}) < \alpha$; $y(\mathbf{r}) > \beta$ define a complementary second phase. In the case $\beta = \infty$ a 1-cut material results; in the case $\beta = -\alpha$ a 2-cut material.

The statistical correlation functions of these materials can be calculated [29, 20, 30]. The volume fraction is given by $p = (2\pi)^{-\frac{1}{2}} \int_{\alpha}^{\beta} e^{-\frac{1}{2}t^2} dt$ and the two point correlation function is

$$p_2(r) = p^2 + \frac{1}{2\pi} \int_0^{g(r)} \frac{dt}{\sqrt{1-t^2}} \times \left[\exp\left(-\frac{\alpha^2}{1+t}\right) - \exp\left(-\frac{1}{2} \frac{\alpha^2 - 2\alpha\beta t + \beta^2}{(1-t^2)}\right) + \exp\left(-\frac{\beta^2}{1+t}\right) \right]. \quad (4)$$

Here $g(r) = \langle y(0)y(\mathbf{r}) \rangle$ is the field-field correlation function and is related to the spectral density of the field

$$g(r) = \int_0^{\infty} P(k) \frac{\sin kr}{kr} dk. \quad (5)$$

In terms of the normalized 2-point function $\gamma(r) = (p_2(r) - p^2)/(p - p^2)$ it can be shown that [20]

$$1 - \gamma(r) \sim (1 - g(r))^{\frac{1}{2}} \quad r \rightarrow 0 \quad \& \quad \gamma(r) \sim g(r) \quad r \rightarrow \infty. \quad (6)$$

Higher order correlation functions can also be evaluated for level-cut GRF media [31, 32, 18]. The freedom in specifying α , β and $P(k)$ (or $g(r)$) allows a wide variety of materials to be modelled.

4 Surface fractals

Recent microstructural studies of composite steels [2] have revealed a fractal boundary between a ferrite and pearlite phase. Using a scaling relationship between the area and perimeter of the pearlite grains it was found that $d_f \approx 1.5$. In three-dimensions this implies a surface fractal dimension of $D_s = 1 + d_f \approx 2.5$. Small angle scattering studies have shown that lignite coal [21] has $D_s \approx 2.5$ and sedimentary sandstones have $2.25 \leq D_s \leq 2.96$ with many exhibiting $D_s = 2.5 \pm 0.1$ [1]. Materials with such a fractal surface can be generated in the GRF scheme by using, for example, $g(r) = e^{-r/l}$ where l is a pore/grain length scale which we normalize to unity. In this case $1 - \gamma(r) \sim r^{\frac{1}{2}}$ as $r \rightarrow 0$ so that $D_s = 2.5$. The corresponding spectral density is

$$P(k) = \frac{4k^2}{\pi(1+k^2)^2}. \quad (7)$$

To account for the fact that physical surfaces only exhibit fractal scaling down to some finite length scale (e.g. the lattice constant) a cut-off length can be introduced in the model by setting $P(k) = 0$ for $k > K$ (and scaling so $\int P(k)dk = 1$). This leaves the large scale microstructure unchanged and filters out the high frequency (rougher) sinusoids in Eqn. (3) above a length scale $2\pi/K$. The magnitude of K is estimated from experimental studies. In ferritic-pearlite steels [2] the minimum scale reported is $.1\mu m$ and the grain size is $O(50\mu m)$ so $K \approx 2\pi 50/.1 = 3.1 \times 10^3$. In sandstones [1] the minimum scale measured is $.5 \times 10^{-3}\mu m$ and the pore-size is around $10\mu m$ so $K \approx 2\pi 10/.0005 = 1.3 \times 10^6$. We assume $K = \infty$ provides a reasonable model of fractal steel and sandstone interfaces. To clearly demonstrate the effect of a fractal surface on material properties we also consider materials with $K = 8$ (providing a smooth interface with $D_s = 2$).

Cross sections of the surface fractal material are shown in Figs. 1 (a) & (b). The morphology of the 2-cut field is very similar to that observed in steel composites [2]. The roughness of the interface for the 1-cut case is clearly visible in Fig. 2. The spectral density and associated 2-point correlation function of each of the materials are shown in Fig. 3. Ten two-dimensional realizations of each model are calculated from Eqn. (3) for the case $\alpha = 0$ & $\beta = \infty$ ($p = \frac{1}{2}$). The average value of $\gamma(r)$ is represented by symbols in this figure: the fractal scaling of $\gamma(r)$ is evident.

To determine the effect of the fractal microstructure on the conductivity and elastic moduli of each material we evaluate the microstructure parameters for both models ($K = \infty, 8$). The results are given in Tables 1 & 2 and bounds on the shear moduli are shown in Fig. 4 for the case where the shear and bulk moduli are both equal to 1 in phase 1 and 0 in phase 2. Note that the lower bound vanishes at this

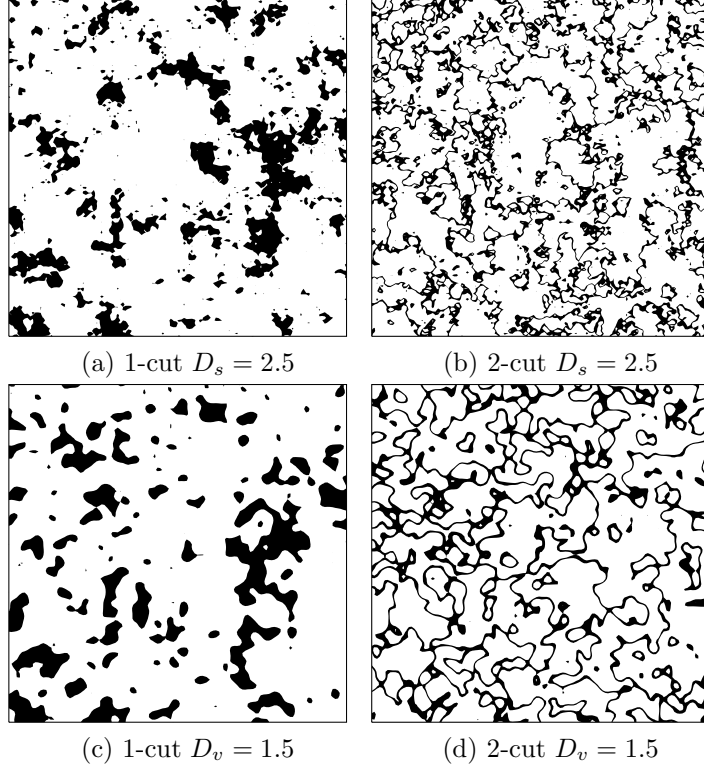


Figure 1: Cross-sections of the fractal composites generated using Eqn. (3). The black region corresponds to Phase 1 at a volume fraction $p = 0.2$. In the 1-cut case $0.84 < y(r) < \infty$ and in the two cut case $-0.25 < y(r) < 0.25$.

contrast. Curves for the bulk moduli and conductivity are qualitatively similar. The shear moduli of the fractal and smooth 1-cut models are quite similar. In contrast the fractal 2-cut model has a significantly reduced resistance to shear when compared to the smooth 2-cut model: a rough interface decreases the elastic strength of a material if the inclusion phase is stronger than the bulk phase. This result is similar to a trend observed in composite steels: an increase in D_s leads to a decrease in impact toughness.

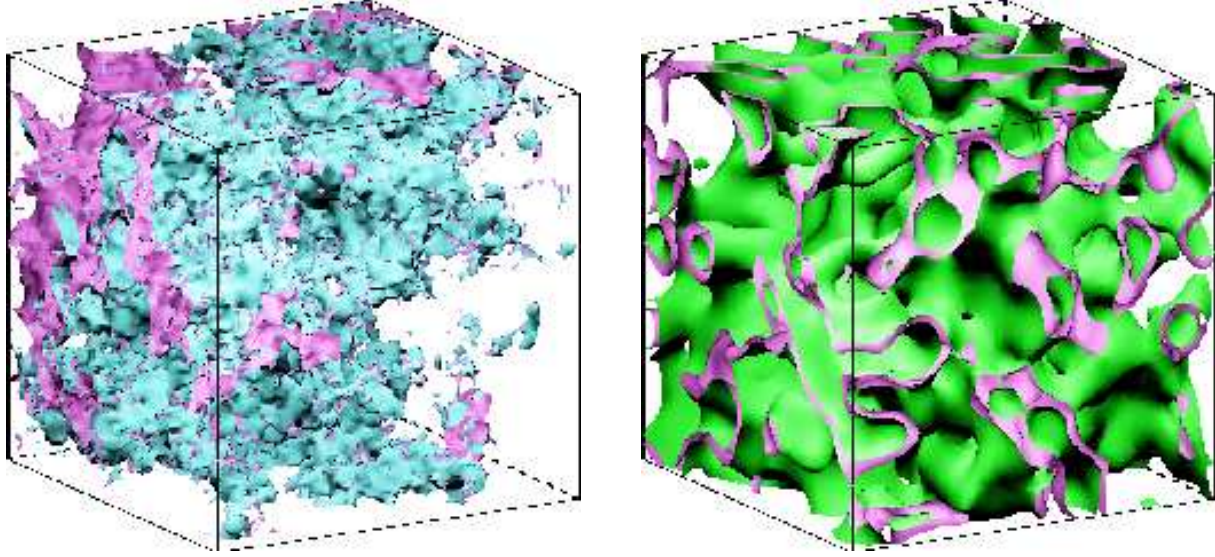


Figure 2: The level cut media. (a) A 1-cut surface-fractal interface ($D_s = 2.5$) at $p = 0.22$ ($0.75 < y(r) < \infty$); (b) A 2-cut volume-fractal ($D_v = 1.5$) at $p = 0.2$ ($-0.25 < y(r) < 0.25$).

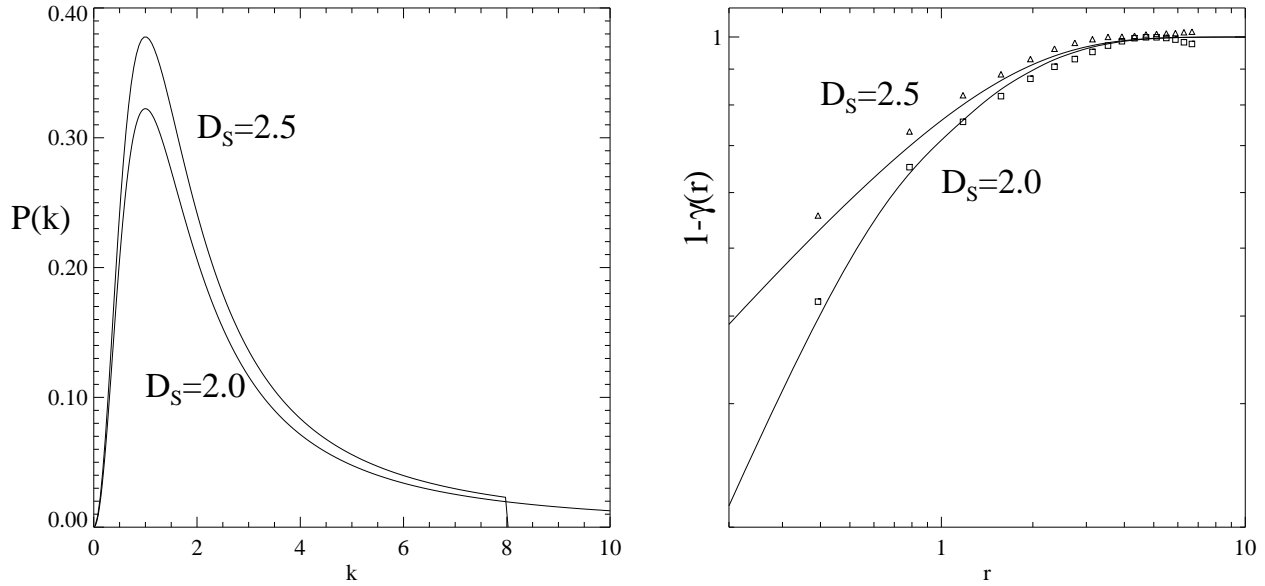


Figure 3: The spectral density and normalized 2-point correlation function of the 1-cut surface fractal media ($p = \frac{1}{2}$). The symbols represent computational measurements of $\gamma(r)$ averaged over 10 cross-sections.

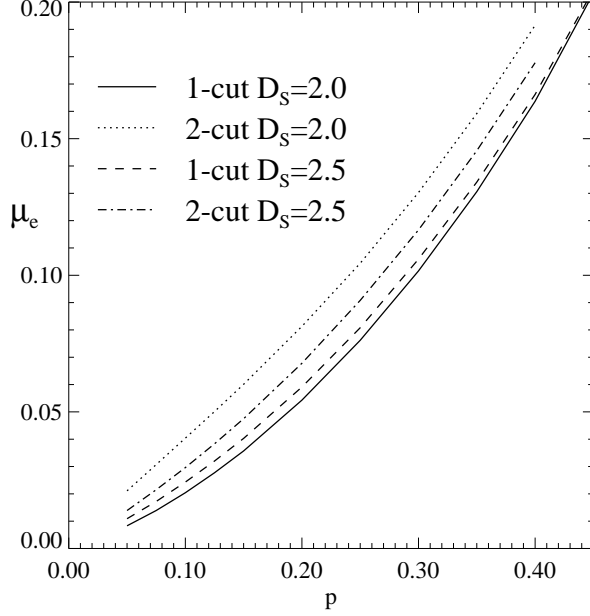


Figure 4: Upper bounds [13] on the shear modulus of the surface-fractal media.

5 Volume fractals

Aerogels provide good examples of volume fractal materials with $D_v \approx 2$ [4]. The formation process has been modelled by the cluster-cluster aggregation model [33, 34, 28] which gives $D_v \approx 1.7 - 1.8$. To see how the level-cut scheme can model volume-fractal materials consider $\gamma(r) \approx C(r/l)^{-A}$ for $r \rightarrow \infty$. The volume of solid within a radius R is [4]

$$\begin{aligned} V(R) &= \int_0^R dv p_2(r)/p = \int_0^R dr 4\pi r^2 ((1-p)\gamma(r) + p) \\ &\approx \frac{(1-p)4\pi C l^A}{3-A} R^{3-A} + p \frac{4\pi}{3} R^3. \end{aligned} \quad (8)$$

Now the former term dominates for $R < R_s = \left(\frac{3(1-p)C}{p(3-A)}\right)^{1/A} l \sim p^{-1/A} l$ where R_s is a saturation scale and $V(R) \sim R^{3-A} = R^{D_v}$. Thus the volume fractal dimension is $D_v = 3 - A$. A simple field-field correlation function which gives rise to this behaviour in the level-cut GRF is

$$g(r) = \left(1 + \frac{2}{A} \frac{r^2}{l^2}\right)^{-A/2}. \quad (9)$$

This field-field correlation function actually leads to a spectral density

$$P(k) = \frac{1}{(2\pi)^3} \int_0^\infty 4\pi r^2 g(r) \frac{\sin kr}{kr} dr \quad (10)$$

which is not strictly positive. Therefore we define a new $P(k)$ which is set to zero for all k beyond the first point K at which $P(k) < 0$ (and re-scale to ensure $\int P(k) dk = 1$). This modification does not change the behaviour of the model at large r . In aerogels l (which we normalize to unity) is related to the length scale of the monomers. In experiments the saturation scale is $O(10\text{nm})$ [4] and in a recent model of a silica gel based on the cluster-cluster aggregation algorithm the saturation scale is around six times the particle diameter at concentrations of $c = 0.05$ [28]. This is consistent with Eqn. (8):

Table 1: *The microstructure parameters the fractal and regular composites for 1-level cut GRF's ($\beta = \infty$).*

	Model							
	$D_s = 2.5$		$D_s = 2.0$		$D_v = 1.5$		$D_v = 3.0$	
p	ζ_1	η_1	ζ_1	η_1	ζ_1	η_1	ζ_1	η_1
0.05	0.294	0.247	0.215	0.165	0.220	0.172	0.197	0.148
0.10	0.319	0.276	0.258	0.212	0.263	0.219	0.243	0.197
0.15	0.342	0.305	0.294	0.253	0.299	0.260	0.281	0.239
0.20	0.366	0.332	0.327	0.291	0.330	0.296	0.316	0.279
0.25	0.388	0.360	0.358	0.327	0.360	0.331	0.348	0.317
0.30	0.411	0.390	0.387	0.363	0.388	0.365	0.380	0.354
0.35	0.433	0.415	0.416	0.396	0.417	0.398	0.411	0.391
0.40	0.456	0.442	0.444	0.431	0.444	0.431	0.441	0.427
0.50	0.500	0.500	0.500	0.500	0.498	0.496	0.500	0.500

Table 2: *The microstructure parameters the fractal and regular composites for 2-level cut GRF's ($\beta = -\alpha$).*

	Model							
	$D_s = 2.5$		$D_s = 2.0$		$D_v = 1.5$		$D_v = 3.0$	
p	ζ_1	η_1	ζ_1	η_1	ζ_1	η_1	ζ_1	η_1
0.05	0.402	0.351	0.786	0.613	0.768	0.589	0.802	0.627
0.10	0.415	0.369	0.706	0.516	0.689	0.500	0.727	0.535
0.15	0.431	0.387	0.656	0.480	0.636	0.450	0.684	0.501
0.20	0.449	0.402	0.628	0.473	0.615	0.470	0.657	0.491
0.25	0.463	0.430	0.612	0.478	0.602	0.473	0.642	0.495
0.30	0.481	0.451	0.605	0.491	0.596	0.488	0.636	0.508
0.35	0.497	0.474	0.603	0.510	0.596	0.506	0.634	0.526
0.40	0.515	0.495	0.607	0.533	0.601	0.529	0.636	0.546

$R_s \sim p^{-1/A} = 0.05^{-1/1.7} = 5.8$. Although the level-cut materials generated using Eqn. (9) has fractal scaling over the correct range of r , it does not necessarily follow that this is an appropriate model for aerogels. It does, however, allow the dependence of properties on D_v to be gauged within the level-cut scheme.

We choose a fractal $A = 1.5$ ($D_v = 1.5$) and non-fractal case $A = 3$ (so the second term in Eqn. (8) dominates and $D_v = 3$) to determine the effect of volume fractal behaviour on material properties. The functions $P(k)$ are shown in Fig. 5. We have generated realizations of the materials using Eqn. (3). Cross-sections of the model for the case $D_v = 1.5$ are shown for the 1-cut and 2-cut cases in Figs. 1 (c) & (d). A three dimensional representation of the 2-cut interface is shown in Fig. 2. The 2-point function of each model has been measured for the case $p = \frac{1}{2}$ and averaged over 50 cross-section realizations of each model. The results, plotted in Fig. 5, show that the level-cut GRF model has volume-fractal scaling.

The microstructure parameters for both $D_v = 1.5$ and $D_v = 3.0$ are given in Tables 1 & 2 and bounds on the conductivity are shown in Fig. 6 for the case $\sigma_{1,2} = 1, 0$ (the lower bounds vanish at this contrast). As we would expect the sheet-like nature of the structures in the 2-cut media are much better conductors than the node/bond-like structures present in the 1-cut media. We find virtually no difference in the fractal and non-fractal materials in both the 1-cut and 2-cut cases. This surprising result suggests that the properties of volume-fractal composites (such as aerogels) are not explicitly dependent on the fractal dimension.

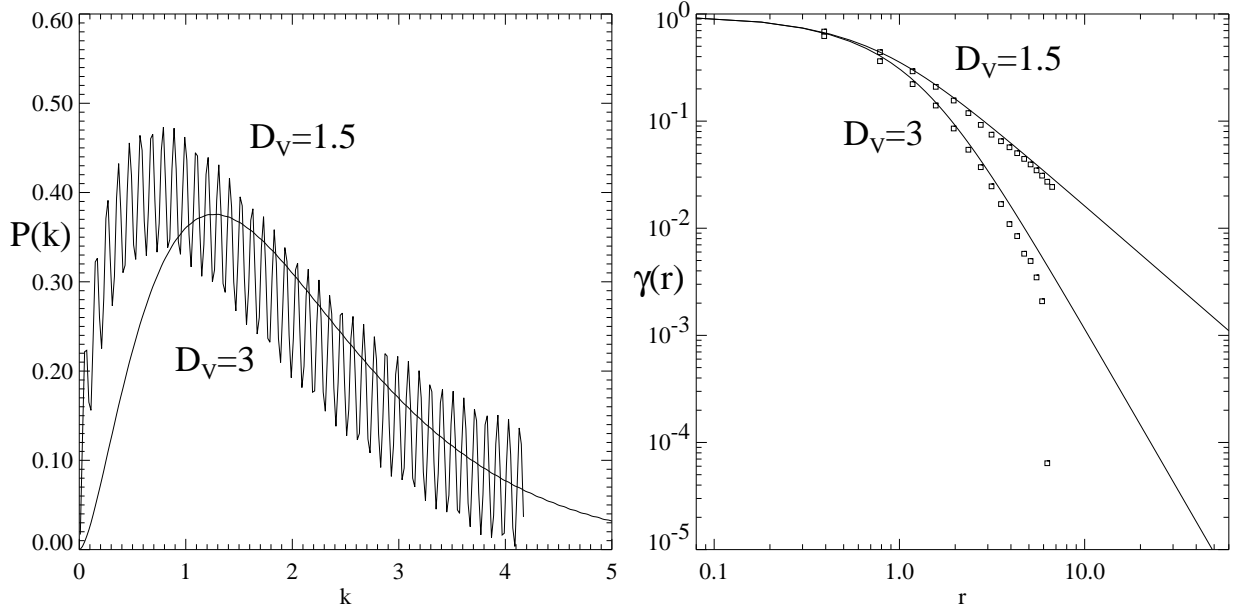


Figure 5: The spectral density and normalized 2-point correlation function of the 1-cut volume fractal media ($p = \frac{1}{2}$). The symbols represent computational measurements of $\gamma(r)$ averaged over 50 cross-sections.

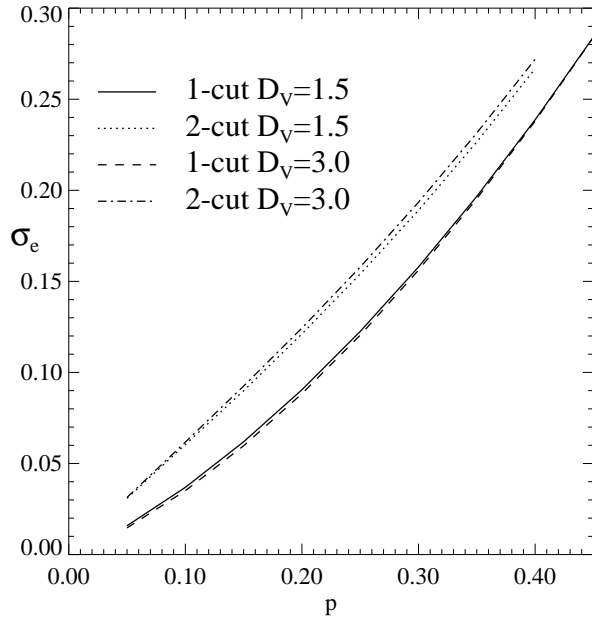


Figure 6: Upper bounds [9, 15] on the conductivity of the volume-fractal media.

6 Conclusion

We investigate the influence of fractal structure on material properties. We have calculated rigorous bounds on the conductivity and elasticity of fractal media generated using the level-cut random field model. The behaviour of the bounds indicates that a fractal interface plays a minimal role in the properties of 1-cut media. For the two-cut model, which mimics the microstructure of both foams [19] and porous rocks [18] a much stronger influence is observed. In contrast, varying the volume-fractal dimension of both 1-cut and 2-cut media has little effect on the property bounds. The latter result indicates that the remarkable properties [35] of aerogels are influenced more by the fact that they contain very well connected structures at high porosities, rather than their fractal characteristics [4, 28]. In the future we shall utilise a range of microstructural studies [28] to develop a more appropriate model of aerogel structure. This will allow a more rigorous comparison between model and experimental properties.

References

- [1] P.-Z. Wong, J. Howard, and J.-S. Lin, Phys. Rev. Lett. 57 (1986) 637.
- [2] H. Su, Z. Yan, and J. T. Stanley, J. Mat. Sci. Lett. 14 (1995) 1436.
- [3] B. M. Smirnov, Phys. Rep. 188 (1990) 1.
- [4] D. W. Schaefer and K. D. Keefer, Phys. Rev. Lett. 53 (1984) 1383.
- [5] Y. Kantor and D. J. Bergman, J. Phys. A 18 (1985) L861.
- [6] P. M. Adler and J. F. Thovert, Fractal Porous Media 13 (1993) 41.
- [7] L. M. Schwartz, P. N. Sen, and D. L. Johnson, Phys. Rev. B 40 (1989) 2450.
- [8] M. Sahimi, Rev. Mod. Phys. 65 (1993) 1393.
- [9] M. Beran, Nuovo Cimento 38 (1965) 771.
- [10] G. W. Milton, J. Appl. Phys. 52 (1981) 5294.
- [11] M. Beran and J. Molyneux, Q. Appl. Math. 24 (1966) 107.
- [12] J. J. McCoy, *Recent Advances in Engineering Science*, (Gordon and Breach, New York, 1970).
- [13] G. W. Milton and N. Phan-Thien, Proc. Roy. Soc. London A 380 (1982) 305.
- [14] S. Torquato, Appl. Mech. Rev. 44 (1991) 37.
- [15] G. W. Milton, Phys. Rev. Lett. 46 (1981) 542.
- [16] W. F. Brown, J. Chem. Phys. 23 (1955) 1514.
- [17] M. A. Knackstedt and A. P. Roberts, Macromol. 29 (1996) 1369.
- [18] A. P. Roberts, *Diffusion-controlled growth and transport in random composites*, PhD thesis, Australian National University, 1995.
- [19] A. P. Roberts and M. A. Knackstedt, J. Mat. Sci. Lett. 14 (1995) 1357.
- [20] N. F. Berk, Phys. Rev. A 44 (1991) 5069.
- [21] H. D. Bale and P. W. Schmidt, Phys. Rev. Lett. 53 (1984) 596.
- [22] D. Avnir, D. Farin, and P. Pfeifer, J. Chem. Phys. 79 (1983) 3566.

- [23] P. W. Schmidt et al., J. Chem. Phys. 90 (1989) 5016.
- [24] F. Bartoli et al., J. Soil Science 42 (1991) 67.
- [25] G. Korvin, *Fractal Models in the Earth Sciences*, (Elsevier, Amsterdam, 1992).
- [26] P. zen Wong and Q. zhong Cao, Phys. Rev. B 45 (1992) 7627.
- [27] L. G. B. Bremer et al., Adv. Colloid Interface Sci. 46 (1993) 117.
- [28] A. Hasmy et al., Phys. Rev. B 50 (1994) 6006.
- [29] N. F. Berk, Phys. Rev. Lett. 58 (1987) 2718.
- [30] M. Teubner, Europhys. Lett. 14 (1991) 403.
- [31] A. P. Roberts and M. Teubner, Phys. Rev. E 51 (1995) 4141.
- [32] A. P. Roberts and M. A. Knackstedt, Unpublished.
- [33] P. Meakin, Phys. Rev. Lett. 51 (1983) 1119.
- [34] M. Kolb, R. Botet, and R. Jullien, Phys. Rev. Lett. 51 (1983) 1123.
- [35] X. Lu et al., Science 255 (1992) 971.